Thirty Years of Change in Forest Soils of the Allegheny Plateau, Pennsylvania

S. W. Bailey,* S. B. Horsley, and R. P. Long

ABSTRACT

Numerous studies have investigated the potential depletion of available base cation pools from forest soils in regions impacted by acid deposition. However, these studies mostly used indirect methods. Retrospective studies, providing direct evidence of chemical changes in forest soils, are relatively rare due to a lack of appropriate sampling, documentation, and archiving of samples over decadal or longer periods. We were provided an unusual opportunity to conduct such a retrospective study with relocation of four sites on the Allegheny Plateau in Pennsylvania. Detailed soil sampling and analyses were conducted in 1967. An original investigator was available to insure field sampling protocol consistency during resampling in 1997, and the original samples had been archived and were available for reanalysis. At all four sites there were significant decreases in exchangeable Ca and Mg concentrations and pH at all depths. Exchangeable Al concentrations increased at all depths at all sites, however increases were only significant in upper soil horizons. Short-term temporal changes, estimated by sampling the Oa/A horizon annually for 3 yr, were insignificant, suggesting that the differences between 1967 and 1997 are part of a long-term trend. At most of the sites losses of Ca and Mg on a pool basis were much larger than could be accounted for in biomass accumulation, suggesting leaching of nutrients off-site.

THERE IS MUCH INTEREST in possible depletion of base cations, particularly Ca, from forest soils (Federer et al., 1989; Likens et al., 1996, Binkley and Hogberg, 1997; Huntington, 2000). Consequently, there is heightened interest in the role that base cation nutrients play in forest health and productivity. Leaching of foliar membrane Ca and Al-induced Ca deficiency have been linked to decline of red spruce (*Picea rubens* Sarg.) (Lawrence et al., 1997; Shortle et al., 1997; DeHayes et al., 1999). In Europe, Mg deficiency has been associated with decline of Norway spruce [*Picea abies* (L.) H. Karst] (Hüttl, 1993). Imbalanced base cation nutrition, coupling low availability of Ca and Mg with high levels of Al and Mn have been correlated with predisposition of sugar maple (*Acer saccharum* Marsh.) to decline disease (Horsley et al., 2000). Experimental additions of dolomitic lime have increased crown vigor, growth, flower, and seed production and decreased mortality of sugar maple on the Allegheny Plateau in Pennsylvania (Long et al., 1997; Long et al., 1999) and in eastern Canada (Moore et al., 2000).

Yet, direct evidence of base cation depletion from forest soils remains rare. Calcium depletion as a result of atmospheric acid deposition is supported on theoretical grounds (Reuss, 1983), by laboratory experiments (Lawrence et al., 1999), by observational mass balance studies (Bailey et al., 1996; Likens et al., 1996; Huntington et al., 2000) and by experimental acidification studies (Fernandez et al., 2003). Retrospective studies commonly have not shown reductions in exchangeable bases, often in contrast to concurrent mass balance studies (Johnson et al., 1997; Likens et al., 1998). One retrospective study, which has documented base cation depletion was performed at the Calhoun Experimental Forest in South Carolina in a loblolly pine stand on postagricultural (previously limed) land. Here, Markewitz et al. (1998) used a hydrogen budget approach to determine that 38% of the observed base cation depletion was due to acid deposition.

There are several possible explanations for the rare documentation of exchangeable base depletion in retrospective studies. Most retrospective studies are relatively recent, limiting the chance of detecting modest changes in a large pool in the face of spatial variability. Acid deposition is thought to have been widespread across the northeastern USA by the mid-1950s (Cogbill and Likens, 1974; Driscoll et al., 2001). The long-term mass balance model for the Hubbard Brook Experimental Forest (Likens et al., 1996; Bailey et al., 2003) suggests that over the past 50 yr, most of the depletion of soil Ca occurred during the 1970s. Thus studies that were initiated subsequent to this era missed earlier dynamics and must be more sensitive to detect any subsequent changes. Unfortunately, the first soil monitoring study at Hubbard Brook to look beyond the forest floor did not start until 1983 (Johnson et al., 1997).

Moreover, few studies of forest soil base cations in the northeastern USA are suitable to evaluate pre-acid deposition soil bases. Lunt (1932) conducted pioneering studies of forest soil base cations in New England. Lunt's samples were stored for nearly 50 yr before being discarded to make room for a laboratory renovation (W. Shortle, personal communication, 2002). With no archived samples for comparison, and given questions about analytical methodology with Lunt's analyses, it is uncertain that strong conclusions could be drawn from resampling these sites. Heimberger (1934) also conducted analyses of exchangeable base cations during the pre-acid rain era in forest soils of the Adirondack Mountains, New York. Though archived subsamples do not exist, Heimberger left detailed notes of his sampling sites and documented his analytical methods. Modern sampling of Heimberger's plots suggests a strong depletion of exchangeable Ca (Johnson et al., 1994). However, it is not clear that the comparison of Heimberger's methods with modern analytical techniques was ade-

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Abbreviations: dbh, diameter breast height; DD, Dewdrop; FC, Fools Creek; HC, Hearts Content; NB, North Branch.

quate (Lawrence et al., 1997), raising the question of how much Ca has been depleted at these sites.

In 1967, soils representing the dominant soil series and land uses (agriculture, forestry) from 14 sites in Warren County, PA were investigated by the Pennsylvania State University Soil Characterization Laboratory (Ciolkosz et al., 1970). Soil samples were taken by genetic horizon for physical, chemical, and mineralogical analysis; subsamples were archived at the Pennsylvania State University Soil Characterization Laboratory. Six of the sites were forested, while the remaining eight sites were in agricultural areas. We were particularly interested in the forested sites because these archived samples provided an unusual opportunity to evaluate relatively long-term changes in forest soil base cations in a region impacted by acid deposition. At the nearby Kane Experimental Forest, wet sulfate deposition averaged 33 kg ha^{-1} over the period of record (1978–2002); these levels are among the highest measured in the USA (National Atmospheric Deposition Program, 2003).

Four of the forested sites were intact in 1997 and the original soil pit sites were located by original landmarks used to reference the sites; the remaining two forested sites had been disturbed and were not suitable for resampling. In addition to the ability to compare measurements of modern and archived samples, we were able to engage Robert Cunningham, one of the investigators during the 1967 sampling, to resample soils in 1997, 30 yr after the original study. This helped ensure that collection methods were comparable. In this paper we evaluate: (i) short- (1997–1999) and long-term (1967–1997) changes in soil pH, exchangeable Ca, Mg, and Al and (ii) estimate soil cation changes in comparison with net biomass uptake on a site storage basis.

MATERIALS AND METHODS

Research Area

Research areas are located on the Allegheny National Forest in northwestern Pennsylvania. They are within the unglaci-
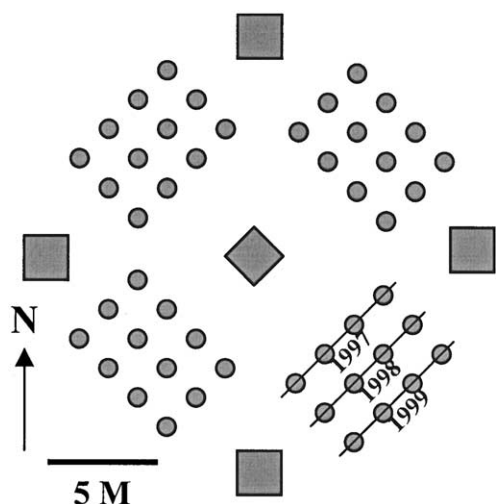

Fig. 1. Sampling layout showing the spatial relationships between the original pit sampled in 1967 (shown as a diamond), the four pits sampled in 1997 (shown as squares), and the forest floor pin-block transects sampled in 1997, 1998, and 1999 (shown as circles).

ated Allegheny High Plateau Section of the Appalachian Plateau Province, 20 to 35 km south of the terminal moraine of the Wisconsin glacial advances (Ciolkosz et al., 1970; Harrison, 1970; McNab and Avers, 1994). The landscape is dominated by contiguous forest with no history of agricultural use. Annual precipitation averages 1067 mm with 550 mm received during the growing season. The area has a humid temperate climate with an average daily temperature of 9°C, and an average growing season of 120 d (Cronce and Ciolkosz, 1983; Kingsley, 1985; McNab and Avers, 1994). Soils are <3 m deep, strongly acid, relatively infertile, developed in residuum derived from sandstone and shale; kaolinite is the dominant clay mineral and is responsible for the relatively low cation exchange capacity.

In 1997, we resampled the four forested sites remaining from the 1967 survey. All sites were in the plateau top physiographic position near the local height of land. The reference names of the four sites, their elevations, map unit designations and taxonomy in the 1967 survey were: (1) Dewdrop (DD) (elev. 628 m), S67 PA 62-6 (1-12), Cookport taxadjunct very stony silt loam, Aquic Fragiudalf, fine-loamy, mixed, mesic; (2) Fools Creek (FC) (elev. 543 m), S67 PA 62-4 (1-14), Cookport very stony loam, Aquic Fragiudult, fine-loamy, mixed, mesic; (3) Hearts Content (HC) (elev. 573 m), S67 PA 62-2 (1-13), Hazleton taxadjunct channery sandy loam, Typic Dystrochrept, loamy-skeletal, mixed, mesic; (4) North Branch (NB) (elev. 622 m), S67 PA 62-5 (1-9), Dekalb channery fine sandy loam, Typic Dystrochrept, loamy-skeletal, mixed, mesic (Ciolkosz et al., 1970).

All four sites supported mature, fully stocked (Stout et al., 1987) second and third growth northern hardwood and mixed oak forests that originated following forest removals between 1890 and 1930 (Marquis, 1975). The overstory trees at DD (basal area: 38.7 m^2 ha^{-1}) were dominated by 90-yr-old (in 1997) northern red oak (*Quercus rubra* L.). A few trees were removed from the stand about 1977, but there has been no other apparent disturbance since then. At FC, the overstory was dominated by 90-yr-old black cherry (*Prunus serotina* Ehrh.) and red maple (*Acer rubrum* L.) containing 33.9 m^2 ha^{-1} of basal area. The 1967 pit site was included in a fertilizer study in 1972, requiring us to locate 1997 sample points approximately 30 m from the outer edge of the fertilizer treatment isolation zone. The overstory at HC (basal area: 32.5 m^2 ha^{-1}) was 100-yr-old mixed oak forest dominated by white oak (*Quercus alba* L.), northern red oak, and red maple. The only apparent disturbance at the site since 1967 was a gypsy moth (*Lymantria dispar* L.) defoliation in 1988 that resulted in mortality of some oak; most of these trees remained standing dead in 1997. The forest stand at NB was dominated by 90-yr-old American beech (*Fagus grandifolia* Ehrh.), black cherry, and red maple with a basal area of 40.8 m^2 ha^{-1}. The original pit site was obliterated by a small gravel pit; 1997 sample points were approximately 30 m away, within the same soil and vegetation.

Sampling

We relocated the 1967 pits from field notes of the original sampling crew. In 1997, four new pits were opened in cardinal directions 10 m from the 1967 pit (when available) (Fig. 1). Soil profiles were described and sampled by genetic horizons according to the same sampling protocols used in the 1967 survey (Ciolkosz et al., 1970). These pit samples were used to evaluate long-term (1967–1997) change in soil chemistry. To determine whether short-term temporal changes could affect assessment of long-term changes in soil chemistry, additional soil samples from upper horizons were taken in 1997, 1998, and 1999. In each of the four quadrants between two adjacent

pits we established three linear transects, each having four potential sample points at 1-m intervals (Fig. 1). One transect in each quadrant was sampled in 1997, 1998, and 1999, respectively. In each of the 3 yr, 10 of the possible 16 sample points were randomly chosen and a 10×10 cm pin-block sample was taken from each point (Federer, 1984). These samples included Oi, Oe, Oa, and A horizons. The underlying E or B horizon was separated from the base of the pin-block and the entire 100 cm^2 sample of each overlying horizon was separated and collected. All samples considered in this study, including the 1967 samples, were collected during July.

Soil Analyses

Soil samples were air-dried and screened to remove particles >2 mm. Samples were then homogenized by mixing via three passes in a riffle splitter. Subsamples for analysis were obtained by riffle sampling and repeated mixing via a plastic scoop to avoid variability induced by separation of soil particles along size or density gradients. Samples were analyzed for pH in 0.01 mol L^{-1} CaCl$_2$ (Robarge and Fernandez, 1987). Organic content was estimated by loss on ignition (Robarge and Fernandez, 1987). Exchangeable cations (Ca, Mg, Na, and K) were determined in 1 mol L^{-1} NH$_4$Cl extracts obtained by mechanical vacuum extraction (Blume et al., 1990). Exchangeable Al was determined in 1 mol L^{-1} KCl extracts. Exchangeable acidity (in the uppermost subdivision of the B horizon) was determined by potentiometric titration of the KCl extracts (Robarge and Fernandez, 1987). Concentrations of all cations in soil extracts were measured with a Varian Vista axial inductively coupled plasma spectrophotometer. Exchangeable Ca and Mg were expressed on an oven-dry mass basis (cmol$_c$ kg^{-1}). Detection limits for our exchangeable cation analyses were equivalent to 0.006 and 0.004 cmol$_c$ kg^{-1} for Ca and Mg, respectively. The few analyses that were below the detection limit were assigned a value of one-half of the detection limit. Triplicate analyses were within 15% of mean values.

Archived subsamples of soils collected in 1967 were analyzed by the same methods used for the new samples. These analyses were compared with the original results (Ciolkosz et al., 1970) to determine comparability of methods. Ciolkosz et al. (1970) used similar methods to analyze pH and exchangeable Al, while exchangeable bases were determined in a pH 7 ammonium acetate extract.

Soil Pools

To evaluate possible causes for observed changes in soil chemical concentrations, soil changes were calculated on a nutrient-pool basis and compared with net storage in biomass uptake. This approach was chosen to evaluate the possible roles of forest growth and leaching on the observed soil changes. We recognize that this approach is not a complete mass balance; inputs via atmospheric precipitation and mineral weathering may vary between the sites and were not considered. Exchangeable Ca, Mg, and Al pools were calculated for each horizon based on measured cation concentrations, horizon thickness, volumetric rock content, and bulk density. Bulk density was measured in sampled clods during the 1967 sampling (Ciolkosz et al., 1970). Values from the original pits were used for similar horizons and depths to estimate bulk density in the 1997 pits. Volumetric rock content was estimated visually from pit faces; the average rock content per horizon for each site was calculated from the observations in all five pits (one in 1967 and four in 1997). The exchangeable pool for each pedon was calculated by summation of the individual horizons to a depth of 140 cm, except at North Branch where

summation was to 100 cm due to relatively shallow bedrock at this site. Soil pools also were summed for a portion of the soil profile approximating the rooting zone—from the Oa/A horizon to either the top of the fragipan (Bx or Btx horizon), or to the top of the C-horizon, in the absence of a root-limiting fragipan. Change in soil storage was estimated by comparing the 1967 pool estimates with the 1997 estimates. The 1967 site pool was calculated with the concentrations of exchangeable cations measured in archived samples, yielding a conservative estimate of nutrient depletion as concentrations of Ca and Mg measured in archived samples were lower than the original analyses. For comparative purposes, the accumulation of Ca and Mg in forest biomass was contrasted with the change in soil pools.

Biomass

Tree biomass in 1997 was estimated from diameter measurements of trees ≥10 cm diameter breast height (dbh) on three 400-m^2 plots at each site. Total aboveground biomass and component biomass were estimated using allometric regression equations. Biomass of each tree was divided into foliage, stem wood, stem bark, branches (including wood and bark), and coarse roots (including wood and bark) using equations compiled by Jenkins et al. (2003). Nutrient concentrations for each species and component were chosen from a literature review (Pardo et al., 2005). Since complete data for all biomass components were not found for most species, a mean value based on the low end of the concentration range for all study species having data was calculated for each component. We used the low-end value as the most conservative estimate of nutrients sequestered in biomass. Total nutrient content in tree biomass was estimated from the products of nutrient concentration and biomass.

To obtain an estimate of 1967 biomass, we used data from eight fully stocked control stands in a thinning study (Nowak 1996) in stands with similar age and species composition to the present study stands and growing on the same plateau top landform. We calculated a mean annual increment for three diameter ranges of each species (10.00–29.00, 29.01–44.50, and >44.50 cm) and extrapolated it to 30 yr. For instance, for black cherry mean diameter growth over 26 yr for trees 29.01-to 44.50-cm dbh was 0.366 cm yr^{-1} or 9.520 cm. For 30 yr this would be 10.985 cm. For black cherry present in our plots in 1997 with dbh ranging from 29.01 to 44.50 cm, 10.985 cm was subtracted from the 1997 diameter to estimate the 1967 diameter of each tree, which was used for subsequent biomass and nutrient content calculations. Biomass, Ca, and Mg content for 1967 were then calculated as described above. The difference between 1997 and 1967 biomass, Ca, and Mg represents a conservative estimate of what was sequestered in trees between these two dates.

Statistical Analysis

Pearson correlation and regression were used to compare the original analysis of soil properties with those obtained by reanalysis of archived samples (Wilkinson, 1997).

Short-term effects of site, year, and the site × year interaction in pin-block samples were evaluated with analysis of variance (ANOVA). Orthogonal polynomial contrasts were used to evaluate trends among the 3 yr of sampling upper horizons. Exchangeable Al concentration was the only soil property that met the ANOVA assumptions of normality and homogeneity of variance; with natural log transformation, exchangeable Ca and Mg data also met ANOVA assumptions. Analyses

of all other soil properties used Friedman's nonparametric ANOVA.

Because horizon sequence and depth varied from pit to pit, temporal change in soil properties were assessed using index horizons, including: the Oa/A, the uppermost subdivision of B, and the horizon sample straddling the 50-cm and 100-cm depths, generally a lower B or BC horizon. Residuals from the two-way ANOVA of year and index horizon were normally distributed only for Al. Calcium, Mg, and pH were evaluated using a t test where the 1997 means were compared with the 1967 value for each site; in this analysis, each horizon was evaluated separately. In all analyses, $\alpha = 0.05$ was the nominal indicator of statistical significance.

RESULTS

New analyses of archived samples were highly correlated with the original analyses published by Ciolkosz et al. (1970) (Fig. 2). Both studies measured pH in a $0.01\ M\ CaCl_2$ solution. The new analyses showed a lower pH than the original analyses, though there was a high correlation between the two ($r = 0.87$). Exchangeable Ca and Mg were measured in a $1\ M$ ammonium acetate (NH_4OAc) solution in the original study and in a $1\ M$ NH_4Cl solution obtained via mechanical vacuum extraction in the current study. Exchangeable Ca and Mg concentrations were lower in the recent measurements; the correlation between the two was high ($r = 0.97$ for Ca; 0.99 for Mg). Exchangeable Al was measured in a $1\ M$ KCl solution in both studies. There was little difference in Al concentrations between the two ($r = 0.92$) (Fig. 2).

Spatial and temporal variations in upper soil horizons were addressed with pit samples collected in 1967 and 1997 and pin-block samples collected in 1997, 1998, and

Fig. 2. **Results of reanalysis of pH (standard units) and exchangeable Ca, Mg, and Al (cmol$_c$ kg^{-1}) in archived soil samples. Original analyses are shown on the x-axes; new analyses, after 30 yr of storage, are shown on the y-axes. The dashed line represents a 1:1 line; solid lines are the regression line describing the relationship between original and new analyses.**

1999 (Fig. 3, Table 1). The Oi and Oe horizons were on average 1 and 2 cm thick, respectively (Table 1). Together the Oa and A horizons were, on average, 1.5 to 2.0 cm thick. While it may have been technically possible to separate an overlying Oa from an underlying A horizon in many profiles, this was impractical due to the combined thin portion of the pedon contributed by these two horizons and would have resulted in insufficient sample for analyses. Therefore, these two horizons were combined for sampling and analyses. Average organic matter content of the Oa/A horizon at each site ranged from 14 to 35% (Table 1), which is within the range of an A horizon, based on an upper limit of 20% organic C content, equivalent to approximately 40% organic matter content (Huntington et al., 1989). Individual pin-block samples showed a normal distribution in organic matter content, with loss on ignition ranging from 5 to 70%. The distribution and range in organic matter content, and thin nature of the forest floor suggest that any break between an Oa and A horizon would be arbitrary with little analytical or ecological significance.

Concentrations of cations in the Oa/A horizon were highest in 1998, while mass and thickness were lowest. This may represent real interannual variation, or that we sampled slightly less deep in 1998, representing an inconsistency in breaking the A from B horizons in the pin-blocks. However, the statistical results show no trends in any parameters from 1997 to 1999 (Table 1). Short-term variability appears minor and within an expected range. The differences in Oa/A chemistry between 1997 and 1999 were much smaller than the differences from 1967 to 1999 (Fig. 3) suggesting that the three-decade differences are part of long-term trends rather than random differences due to short-term variation or sampling errors.

At most sites, and overall, pH, and exchangeable Ca and Mg concentrations were lower while exchangeable Al concentrations were higher in the Oa/A horizon in pit samples collected in 1997 than in 1967 (Fig. 3, Table 2). The mean pH of the Oa/A horizon dropped 0.9 units over the 30-yr period. Exchangeable Ca and Mg were more than four and two times higher, respectively, in 1967 than in 1997. Exchangeable Al was 1.8 times lower in 1967 than in 1997. The combined loss in exchangeable Ca and Mg in the Oa/A over the 30-yr period was 4.1 cmol$_c$ kg^{-1} compared with a gain of 2.6 cmol$_c$ kg^{-1} of Al. The difference may be due to an increase in exchangeable H, which would be consistent with the observed drop in pH, or with a reduction in cation exchange capacity.

There was no difference in pH, Ca, Mg, or Al concentration between pit and pin-block samples collected in 1997 (Al at NB, $p = 0.058$; Mg at HC, $p = 0.067$; Ca at HC, all other comparisons, $p \geq 0.130$) (Fig. 3), suggesting little or no bias in Oa/A chemistry between the two sampling techniques. Pin-block samples collected in 1997, 1998, and 1999 showed minor interannual variation in exchangeable Ca and Mg and among the four sites. There were no trends in exchangeable Ca and Mg as indicated by the orthogonal contrasts (Table 1).
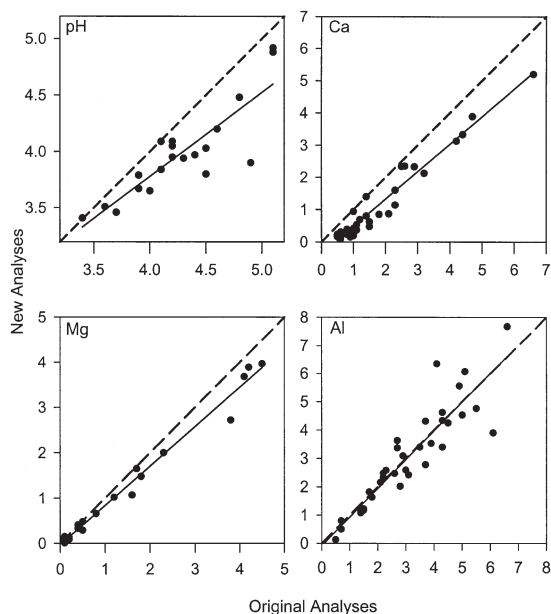
Table 1. Mean (standard deviation) mass, thickness, organic matter, exchangeable element concentrations, pH, and exchangeable element contents, of the Oi, Oe, and Oa/A horizons by site and year derived from 10 cm² pin-block samples of forest floor. Ylin and Yquad are the orthogonal linear and quadratic contrasts among the three years of sampling.

Property	Site†				Year			P-values‡				
	DD	FC	HC	NB	1997	1998	1999	Site	Year	SY	Ylin§	Yquad§
Oi mass, kg m⁻²	1.00 (0.72)	0.91 (0.56)	1.19 (0.62)	0.90 (0.63)	0.71 (0.44)	1.68 (0.49)	0.60 (0.26)	0.002	0.970			
Oi thickness, cm	0.9 (0.6)	0.9 (0.4)	1.2 (0.4)	0.9 (0.5)	0.7 (0.4)	1.2 (0.5)	0.9 (0.4)	0.105	0.949			
Oe mass, kg m⁻²	3.40 (1.83)	2.92 (1.53)	4.23 (1.53)	2.69 (1.33)	3.73 (1.91)	3.35 (1.36)	2.93 (1.58)	<0.001	0.547			
Oe thickness, cm	2.1 (1.1)	2.1 (1.1)	2.6 (1.0)	1.8 (0.9)	2.2 (1.0)	1.9 (0.9)	2.4 (1.2)	0.008	0.473			
Oa/A mass, kg m⁻²	6.98 (3.05)	5.42 (3.35)	13.3 (6.8)	6.78 (4.28)	8.93 (6.43)	6.77 (4.13)	8.59 (5.51)	<0.001	0.958			
Oa/A thickness, cm	1.7 (1.2)	1.3 (0.8)	2.0 (0.9)	2.3 (2.1)	1.7 (1.5)	1.7 (1.2)	2.0 (1.5)	0.011	0.976			
Organic matter, %	29.0 (13.3)	27.6 (13.3)	14.2 (9.2)	35.0 (18.4)	24.3 (15.8)	30.5 (13.6)	24.9 (17.3)	<0.001	0.934			
Ca, cmol$_c$ kg⁻¹	1.2 (1.1)	2.3 (1.6)	0.7 (0.6)	3.1 (2.2)	1.8 (1.9)	2.2 (1.8)	1.6 (1.5)	<0.001	0.025	0.202	0.956	0.007
Mg, cmol$_c$ kg⁻¹	0.52 (0.24)	0.56 (0.25)	0.30 (0.15)	0.64 (.039)	0.52 (0.37)	0.56 (0.24)	0.44 (0.26)	<0.001	0.013	0.444	0.251	0.006
Al, cmol$_c$ kg⁻¹	8.8 (2.2)	7.2 (2.4)	2.5 (1.2)	4.0 (1.6)	5.6 (3.2)	5.7 (3.3)	5.5 (3.0)	<0.001	0.947	0.001	0.912	0.757
pH	3.1 (0.2)	3.3 (0.2)	2.9 (0.1)	3.1 (0.1)	3.2 (0.3)	3.0 (0.1)	3.1 (0.2)	<0.001	0.962			
Ca, g m⁻²	1.4 (0.9)	2.0 (1.3)	1.4 (0.9)	3.6 (2.9)	2.2 (2.1)	2.2 (1.7)	2.0 (1.9)	<0.001	0.991			
Mg, g m⁻²	0.38 (0.16)	0.32 (0.19)	0.41 (0.19)	0.48 (0.42)	0.44 (0.32)	0.38 (0.19)	0.37 (0.27)	0.217	0.999			
Al, g m⁻²	5.3 (2.3)	3.6 (2.6)	2.8 (1.8)	2.2 (1.3)	3.8 (2.6)	3.1 (2.3)	3.4 (2.1)	<0.001	0.984			

† Sites: DD, Dewdrop; FC, Fools Creek; HC, Hearts Content; NB, North Branch.
‡ Analysis of Al concentrations among sites and years was by ANOVA with no transformation; analyses of Ca and Mg concentrations was by ANOVA with a natural log transformation to meet the assumption of homogeneity of variance; analyses of all other soil properties used Freidmans non-parametric ANOVA because even with transformation, data did not meet the assumption of homogeneity of variance. SY, site × year
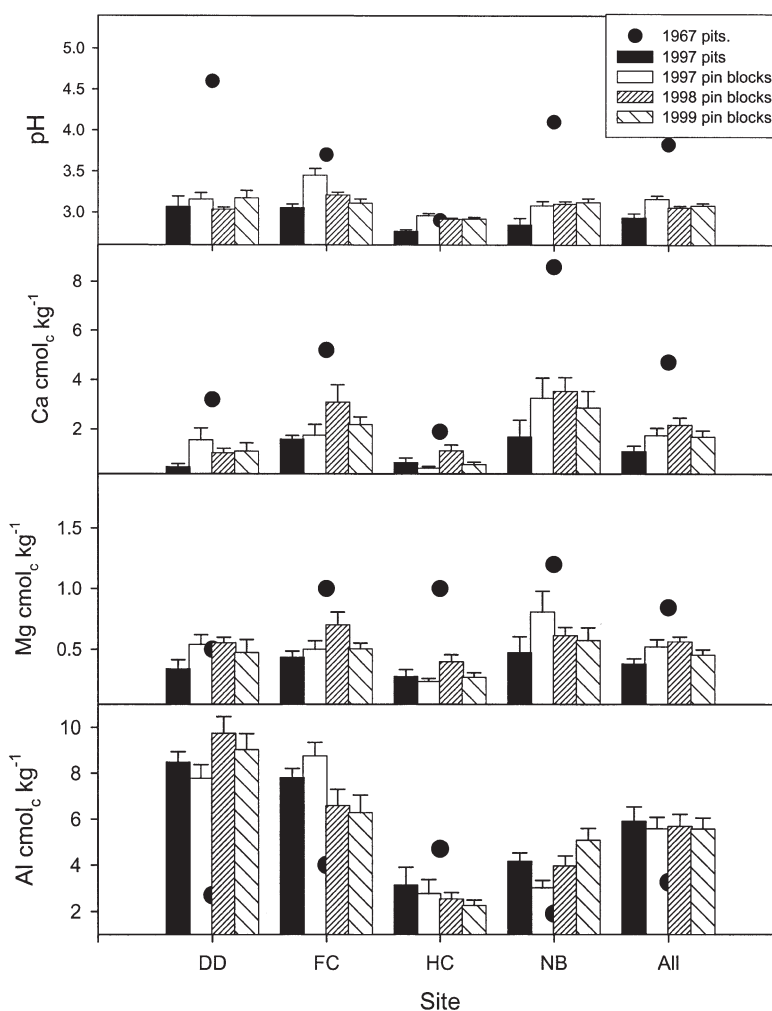§ A significant year quadratic effect indicates that there was not a meaningful year effect.

Fig. 3. Variation in pH (standard units) and exchangeable Ca, Mg, and Al (cmol$_c$ kg⁻¹) in the Oa/A horizon at each of the four study sites, and for all sites combined. The value for the 1967 pits represents a single measurement. The bars represent the mean and standard error of measurements for the 1997 pits (n = 4 per site) and pin-blocks (n = 10 per site, per year). DD, Dewdrop, FC, Fools Creek; HC, Hearts Content; NB, North Branch.

Table 2. Mean (standard deviation) exchangeable element concentrations of Ca, Mg, Al, and pH for the Oa/A, Upper B, B at the 50-cm depth and B at the 100-cm depth horizons in 1967 and 1997.

| | | | | | | | B horizon | | | | | |
| Property | Oa/A horizon | | | Upper B horizon | | | 50-cm depth | | | 100-cm depth | | |
	1967	1997	P	1967	1997	P	1967	1997	P	1967	1997	P
Ca, cmol$_c$ kg^{-1}	4.7 (2.9)	1.1 (0.8)	<0.001	1.1 (0.3)	0.09 (0.06)	<0.001	1.2 (0.7)	0.1 (0.2)	<0.001	2.0 (1.7)	0.2 (0.7)	<0.001
Mg, cmol$_c$ kg^{-1}	0.84 (0.32)	0.38 (0.17)	<0.001	0.11 (0.06)	0.05 (0.02)	<0.001	0.36 (0.56)	0.04 (0.11)	<0.001	1.46 (1.90)	0.15 (0.45)	<0.001
Al, cmol$_c$ kg^{-1}	3.3 (1.2)	5.9 (2.5)	0.016	5.1 (1.2)	7.5 (2.1)	0.025	3.6 (0.9)	3.8 (1.7)	0.799	2.0 (1.6)	2.9 (1.6)	0.409
pH	3.8 (0.7)	2.9 (0.2)	<0.001	3.7 (0.3)	3.5 (0.4)	0.007	4.3 (0.4)	4.0 (0.1)	<0.001	4.2 (0.4)	4.0 (0.1)	<0.001

There were no significant differences among the 3 yr in forest floor horizon mass, exchangeable cation content, thickness, or organic matter content.

The decreases in exchangeable Ca, Mg, and pH and increase in exchangeable Al observed in the Oa/A horizon between 1967 and 1997 were even more pronounced in the underlying mineral horizons, with the contrast extending throughout the depth sampled (Fig. 4). Exchangeable Ca and Mg in mineral soil horizons were 10 times lower in 1997 compared with 1967. Mineral soil pH decreased by 0.2 to 0.3 units while exchangeable Al increased by approximately 50% (Fig. 4). Statistical significance of these differences was tested by comparing 1967 and 1997 results in the upper-most subdivision of the B horizon, immediately below the Oa/A or E-horizon (where present), and the subdivisions of the B horizon at the 50- and 100-cm depths. Reductions in exchangeable Ca, Mg, and pH were significant at all three depths, while the increase in exchangeable Al was significant only in the uppermost subdivision of the B horizon (Table 2).

The average exchangeable acidity in the uppermost subdivision of the B horizon increased from 15.7 cmol$_c$ kg^{-1} in the archived 1967 samples to 19.7 cmol$_c$ kg^{-1} in the 1997 samples. The increase in exchangeable acidity of 4.1 cmol$_c$ kg^{-1} was composed of an increase of 2.4 cmol$_c$ kg^{-1} of exchangeable Al and 1.7 cmol$_c$ kg^{-1} of exchangeable H. Coupled with decreases in exchangeable Ca of 1.0 cmol$_c$ kg^{-1} and exchangeable Mg of 0.06 cmol$_c$ kg^{-1} this resulted in an increase in cation exchange capacity of 3.0 cmol$_c$ kg^{-1}. Base saturation in this horizon decreased from 7.9 in 1967 to 1.4% in 1997. This includes a decrease in Ca saturation from 6.5 to 0.4% and Mg saturation from 0.6 to 0.2%.

Loss of Ca soil pools was approximately an order of magnitude greater than biomass accumulation at DD and FC, about twice as large as biomass accumulation at HC and slightly less than biomass accumulation at NB (Table 3). Loss of Mg soil pools was also more than an order of magnitude greater than biomass accumulation at DD and FC. At HC and NB, estimated biomass accumulation of Mg was somewhat greater than soil pool losses. The Al soil pool increased at all four sites, although the magnitude of the increase varied substantially.

DISCUSSION

Soil Chemical Changes

Quantitative comparison of archived and new soil samples showed a long-term decrease in pH, exchangeable Ca and Mg, and an increase in exchangeable Al. These trends were not observable in short-term comparisons. Our results suggest that an understanding of temporal change in forest soil base cations requires a much deeper sampling effort than commonly has been employed. Changes in pH and exchangeable Ca and Mg were pronounced at all depths sampled (Fig. 4; Table 2), up to a depth of 150 cm. Other studies examining mineral horizons generally have considered only shallower portions of the soil profile. Drohan and Sharpe (1997) found decreases in Oa and A horizon pH over one to three decades in forested sites in Pennsylvania; B horizons were not considered in their study. In other studies where deeper samples were collected, decreases in soil base concentrations were centered on the shallowest horizons. Johnson et al. (1994) found most of the reduction in exchangeable Ca in the Oa and E horizons of Adirondack Spodosols, with no change in exchangeable Ca concentrations in the B or C horizons. In a relatively short-term watershed acidification experiment in Maine, Fernandez et al. (2003) found decreases in pH, Ca, and Mg, and increases in Al in Spodosols beneath softwoods, but not in hardwood stands. These changes were most pronounced in the Oa horizon and upper 5 cm of the B horizon; no change was detected in the remainder of the B horizon, or in the C horizon.

The lack of changes in deeper horizons at these Spodosol-dominated sites (Johnson et al., 1994; Fernandez et al., 2003) may reflect the relative dominance of shallow horizons in contributing to the cation exchange capacity of these younger, glaciated soils. In contrast to the results in the Adirondacks and New England, Markewitz et al. (1998) found significant decreases in pH and exchangeable bases, and increases in exchangeable acidity to a depth of 60 cm in Ultisols in a post-agricultural pine plantation in South Carolina; older samples from greater depths were not available for analysis of temporal change. Our results are more similar to those reported by Markewitz et al. (1998) suggesting that acid deposition may have altered the entire soil profile in these deeper, more highly weathered, unglaciated soils.

In contrast to acid deposition, forest harvesting may not result in detectable depletion of exchangeable bases, as demonstrated in a whole tree harvest experiment at Hubbard Brook Experimental Forest in New Hampshire (Johnson et al., 1997), whole tree and sawlog harvests at Walker Branch Watershed in Tennessee (Johnson and Todd, 1998), and sawlog harvest at Coweeta Hydrologic Laboratory in North Carolina (Knoepp and Swank, 1997). Modeling of biogeochemical changes at Hubbard Brook Experimental Forest since the pre-
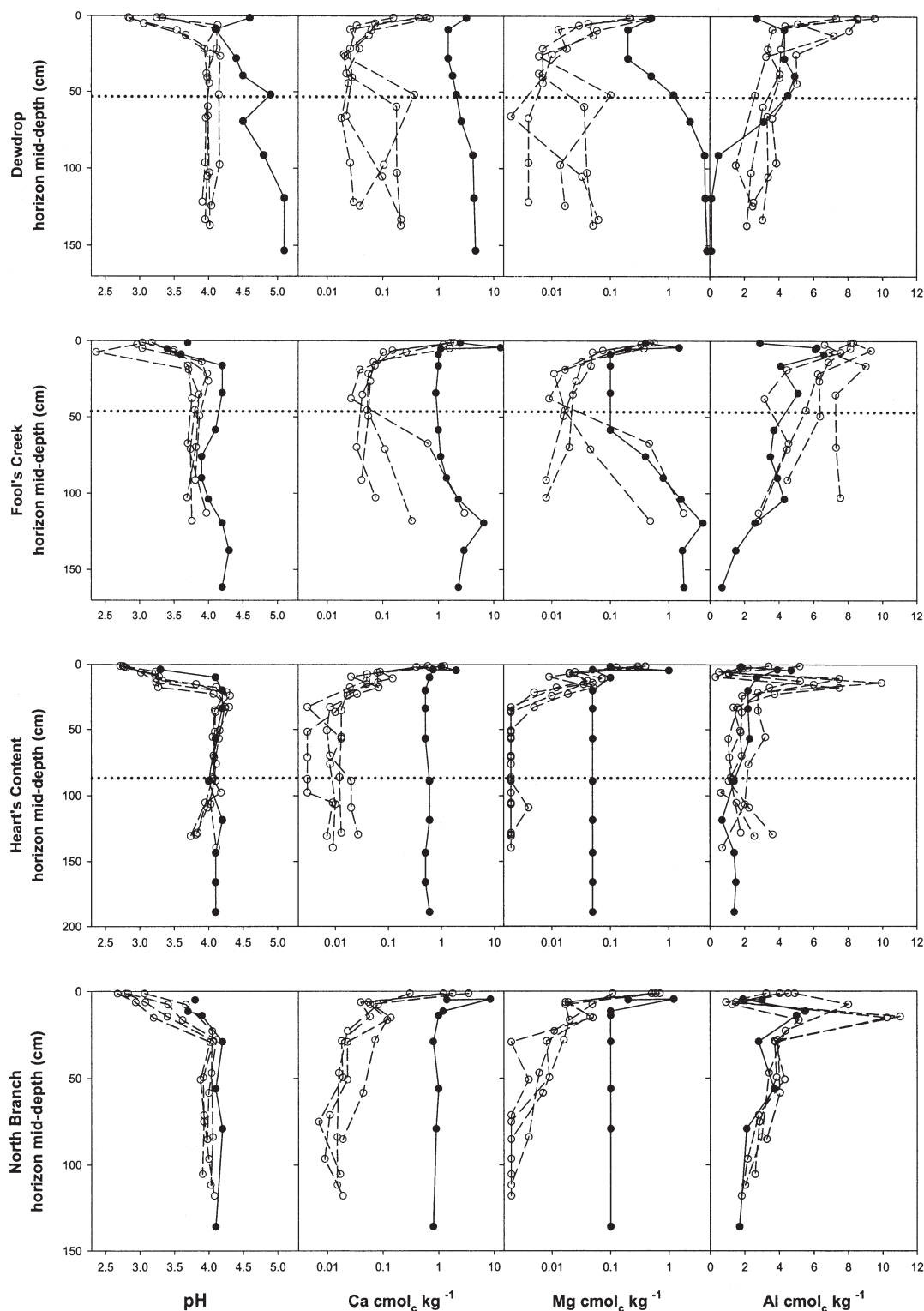
Fig. 4. Depth profiles of pH (standard units) and exchangeable Ca, Mg, and Al (cmol$_c$ kg^{-1}) at each of four study sites. The closed circles represent the data collected from the original pit dug in 1967. The open circles represent the data collected from four pits dug in 1997, located 10 m away from the original pit, in each of the four cardinal directions. The dotted horizontal line shows the average depth of the top of the fragipan, where present. A fragipan was found at three of the five pits at DD, all five pits at FC, and one of five pits at HC.

industrial era suggests that most of the reduction in soil base saturation is due to acid anion deposition, with about 27% of the reduction due to reduced base cation inputs in deposition and little change due to historical

forest disturbance from harvesting or hurricane damage (Gbondo-Tugbawa and Driscoll, 2003).

The observed decreases in exchangeable Ca and Mg may be significant from a forest health perspective. Bai-

Table 3. Change in soil and biomass pools (kg ha^{-1}) from 1967 to 1997. Soil pools are shown to a depth of 140 cm except for NB where they were calculated to the 100-cm depth due to shallow bedrock. Note Al accumulation in biomass was not calculated.

Site	Property	Ca	Mg	Al
DD	soil (140 cm)	−5916	−3759	927
	biomass	421	34	
FC	soil (140 cm)	−2658	−854	2075
	biomass	327	34	
HC	soil (140 cm)	−732	−20	154
	biomass	325	27	
NB	soil (100 cm)	−359	−16	711
	biomass	499	40	

ley et al. (2004) proposed threshold values for Ca and Mg saturation in the upper B horizon of 2 and 0.5%, respectively. Sugar maple growing in soils with values less than these threshold levels was susceptible to decline disease on the Allegheny Plateau. In the present study, the average values of both Ca and Mg saturation were above this threshold in 1967 and below in 1997, consistent with the occurrence of widespread sugar maple decline in this region in the 1980s and 1990s.

Biomass plays a role in storage of base cations on site by sequestering them in plant tissue and organic residues. However, comparison of soil pool changes with net biomass accumulation suggests that much of the change in exchangeable Ca and Mg in these soils cannot be accounted for by forest growth, implying off-site leaching. This is consistent with studies that have suggested that acid deposition has induced significant losses of exchangeable base cation pools by hydrologic leaching (Likens et al., 1996; Huntington et al., 2000; Fernandez et al., 2003).

Techniques for Retrospective Studies

Careful documentation of field and laboratory methods and results, archiving of samples, and lack of recent disturbance opened the possibility to explore changes in forest soil base cations over three decades at sites that receive relatively large loads of acid deposition, and are in landscapes considered especially sensitive to acid deposition impacts based on geological and pedological factors (Levine and Ciolkosz, 1988). Although methods of analysis were similar, reanalysis of archived samples revealed important differences in the analytical results between the two sets of measurements. Such differences might be attributed to changes in the samples with aging, or differences between analytical methods. The high correlation between the two sets of measurements suggests that analytical differences are more important as changes induced by aging might not be expected to have such a regular effect on samples of widely differing properties (e.g., organic content, texture). The difference in pH and exchangeable Al measurements between the archived soil and the original 1967 measurements was very small on an absolute basis, as well as compared with the changes inferred by comparing the results from the 1997 sampling with the original data. The mean difference between exchangeable base measurements in the two studies was somewhat

larger, with the recent analyses consistently showing lower concentrations than the original results. Part of this difference appears to be due to a difference in detection limits. In 1970, Ciolkosz et al. did not report exchangeable Ca or Mg concentrations <0.5 and 0.1 cmol$_c$ kg^{-1}, respectively, whereas we were able to measure exchangeable Ca and Mg as low as 0.006 and 0.004 cmol$_c$ kg^{-1}, respectively. Taking advantage of improvements in analytical detection limits with advances in instrumentation, and assessing the differences between methods and laboratories are critical features of retrospective studies of soil properties, that would not be possible without long-term archiving of soil materials.

Although the reanalysis of archived samples shows consistent differences with the original analyses, the differences are small compared with the contrast of 1997 and 1967 samples (Fig. 2 and 4), indicating large decreases in exchangeable base cation concentrations over three decades. Other studies have not detected changes in base cation storage in forest soils exposed to acid deposition (e.g., Johnson et al., 1997; Johnson and Todd, 1998; Yanai et al., 1999). This finding could be attributable to the difficulty in detecting change due to large spatial variability of forest soil properties, to the short duration of retrospective studies relative to the rate of change in base cations, or the initiation of retrospective studies after adjustment in soil base cations to the acid deposition regime had already occurred.

Rocky forest soils generally are considered to be among the most spatially heterogeneous. However, spatial variability of chemical concentrations among the four 1997 pits at each site was small (Fig. 4, Table 2). Several techniques employed in this study may have contributed to the appearance of low spatial variability between sites. Sampling by genetic horizon, by definition, combines sample material that has undergone similar pedogenic and biotic influences. Differences in color, texture, root density, etc. all are used as indications of pedogenic horizons, and thus used to divide material for sampling purposes. In contrast, sampling by depth increment can lump together very heterogeneous materials. For example, a sample of the upper 10 cm of mineral soil may contain almost any combination of A, E, Bhs, Bs, or Bw horizons, each with distinct organic matter contents, and soil particle surface coatings—factors that will greatly affect the results of a pH or exchangeable cation analysis, depending on how much of a given horizon contributes to a sample. A second field-sampling factor that may have contributed to low spatial variability is that large samples were collected. Within a given genetic horizon, sample was collected from all four faces of the pit, totaling approximately 2 kg of total mass. In contrast, if only the amount of sample needed for analysis was collected—<50 g for the parameters we measured—it would be more likely to obtain material biased by very small-scale variations within a genetic horizon. Finally, careful sample homogenization and subsampling in an unbiased manner in the laboratory, such as the rigorous riffle sampling procedures we employed, may remove much variability in-

troduced in the laboratory that has been traditionally blamed on spatial variability in the field.

Some investigators have focused retrospective sampling efforts on the forest floor (e.g., Yanai et al., 1999), as this portion of the soil profile has the greatest root density and is often considered to be most important to forest biogeochemical processes and nutrition. However, for forested soils such as those studied here, the interpretation of forest floor dynamics may be hindered by difficulty in distinguishing the boundary between the Oa and A horizons, that is, distinguishing the base of the forest floor. In our study, this break seems artificial and not justified by a difference in processes or ecological importance. One solution may be to include the A in forest floor sampling programs, as it is generally easier to distinguish between an A and an E or B horizon than it is to distinguish between an Oa and an A horizon.

CONCLUSIONS

There were long-term decreases in pH, exchangeable Ca, and exchangeable Mg concentrations and increases in exchangeable Al concentration at all depths between two sampling periods separated by 30 yr. Significant short-term changes were not observed by resampling surficial horizons over three sequential years.

Comparisons of soil change on a soil pool basis with net biomass accumulation suggested substantial leaching of Ca and Mg off-site in most cases. Expression of Ca and Mg losses as a saturation value suggests that sometime over the past 30 yr these sites crossed a threshold where sugar maple may be sensitive to decline disease. This is consistent with widespread occurrence of decline in this region during the 1980s and 1990s.

Careful documentation of study location, field and laboratory procedures, and archiving of original soil samples allowed for a detailed retrospective study of soil change that removed many of the questions that have plagued such efforts in the past. Although rocky soils are considered to be too spatially variable to detect temporal changes, we found little variability in soil base cation concentrations within sites. This may have been due to careful sampling by genetic horizons, collection of large samples, and careful application of laboratory subsampling procedures. Changes in soil base cations were pronounced at all depths sampled, up to 1.5 m, suggesting that whole pedon analysis is needed to fully understand dynamics in forest soils.

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